The Generalized Thermodynamic Temperature and the New Expressions of the First and the Second Law of Thermodynamics

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The classical thermodynamics reflects the significant relationship between the heat and the temperature. On the basis of the relationships, according to the mathematical derivation, this paper structures the conceptions of generalized heat, generalized thermodynamic temperature, generalized entropy and so on. The series of conceptions in the classical thermodynamics is merely a special case of the generalized thermodynamics. Based on these conceptions of generalized thermodynamics, this paper presents the new expressions of the first law and the second law of thermodynamics. In other words, these expressions are endued with new explanations. The Eq. $LZ = kTS$ given by this paper provides theoretical basis for these new expressions.

Introduction

In the historical development of thermodynamics, internal energy is introduced as a deduction of the first law of thermodynamics. Some researchers (including this paper) consider the internal energy as the nonfinite initial definition. According to the first law of thermodynamics, internal energy is defined by Eq. (1.1).

$$\mathrm{d}U = \delta Q - \delta W, \tag{1.1}$$

In Eq. (1.1), the definition of δW could be given by other physical subjects, there is no doubt about it. But we think the definition of δQ in thermodynamics has some defects. In the famous Joule's equivalent experiment, Joule used electricity to heat the water. He found that the electric power was in proportion to the incremental temperature. As the development of the heat engine, there were abundant data of the water heating, and the heat which could increase the temperature of 1 gram of water by 1℃ was defined as 1 Cal. Therefore, by its nature, the definition of heat is presented that heat is energy depended on the difference in temperature between the thermodynamics system and the outside to transfer. To some extent, the relationship of heat and temperature is like the relationship of flux and gradient or the relationship of electric energy and electrical potential force. It also means that the measurement of heat is relied on the measurement of temperature.

In classical thermodynamics, temperature is determined by the zeroth law of thermodynamics. But the temperature scale which is determined the value of the temperature could not be given by the zeroth law. The conception of thermodynamic temperature scale is founded

Nomenclature

U = internal energy, J

u = specific internal energy, J/kg

Q = heat, J

q = specific heat, J/kg

S = entropy, J/K

s = specific entropy, J/(kg·K)

T = temperature, K

W = work, J

w = specific work, J/kg

V = volume, m³

v = specific volume, m³/kg

P = pressure, Pa

U_k = generalized internal energy, J

u_k = specific generalized internal energy, J/kg

Φ = generalized heat, J

φ = specific generalized heat, J/kg

Z = generalized entropy, J/ $K^{1/k}$

ζ = specific generalized entropy, J/(kg·$K^{1/k}$)

L = generalized temperature, $K^{1/k}$

k = thermodynamic temperature transformation ratio

Z_e = generalized entropy production, J/ $K^{1/k}$

by the second law of thermodynamics and the conception of reversible cycle, it is also called thermodynamic temperature or absolute temperature. According to the Carnot law, two different thermodynamic temperatures working in two different heat reservoirs could be defined by Eq. (1.2).

$$Q_1/Q_2 = h(t_1)/h(t_2) = T_1/T_2, \qquad (1.2)$$

Thus the problem returns, the measurement of temperature is relied on the measurement of heat. This question is the inherent contradictions of the classical thermodynamics. In this paper, we call it "Twine of temperature and heat". This problem does not testify the thermodynamic temperature is wrong. It guides us to query the uniqueness of thermodynamic temperature.

Obviously, a simple way to solve the "Twine of temperature and heat" is to prove the thermodynamic temperature is unique, is the real absolute temperature. But as the foregoing discussion has shown, the definition of classical thermodynamic temperature could not prove the uniqueness of thermodynamic temperature. Caratheodory raised another method to determine thermodynamic temperature. He thought thermodynamic temperature is the reciprocal of energy integrating factor occurred in thermal process between two equilibrium states.

According to the first law of thermodynamics, we can conclude the Eq. (1.3).

$$\delta Q = dU + \delta W, \qquad (1.3)$$

On the basis of the property of the perfect differential, there must be an integrating factor $1/T$, which makes S to be a perfect differential and satisfies Eq. (1.4).

$$\delta Q/T = dU/T + \delta W/T = dS, \qquad (1.4)$$

This status parameter is just the thermodynamic entropy, and for the existence of integrating factor, the process must be reversible. So according to the definition of the temperature by Caratheodory, is the thermodynamic temperature unique?

Since the temperature is a perfect differential function, by the property of perfect differential, multiply a perfect differential function by a perfect differential function, the consequence is still a perfect differential function. For example, d(TP) is still a perfect differential function. It is not difficult to prove that, if $1/T$ is an integrating factor, $1/(TP)$ is still an integrating factor. As there are infinite status parameters which fit the integrating factor requirement, this definition still cannot solve the uniqueness problem of thermodynamic temperature.

So can we determine a unique thermodynamic temperature by experiment? Now let's review the relevant history. The simplest empirical temperature scale is ideal gas temperature scale. Early in the 17th century, Boyle (1662) and Mariotte (1667) found that the gas specific volume is inversely proportional to the gas pressure when the gas temperature is invariant. Charley pointed out that when the gas volume is fixed, the gas pressure change is in proportion to the gas temperature change. Gay-Lussac experiment showed that, in the condition of constant volume, gas pressure change is in proportion to gas temperature change. According to these consequences, we can determine a new temperature scale-- ideal gas temperature scale. Suppose that for some given volume gas, when gas temperature is 100℃, the gas pressure is p_1, when gas temperature is 0℃, the gas pressure is p_2. Then we can get

$$\Delta t/\Delta p = 100/(p_1-p_2) = 100/[p_2\times(p_1/p_2-1)] = const, \quad (1.5)$$

If we define the following rules, when $p_2\rightarrow 0$, $T_2\rightarrow 0$ and the temperature unit is the same as celsius temperature scale. Then,

$$T_1/T_2 = P_1/P_2, \qquad (1.6)$$

$$(T_1-T_2)/(P_1-P_2) = \Delta t/\Delta p = T_2/P_2, \qquad (1.7)$$

Enormous gas experiments show that, when the gas pressure is minimal, we can get Eq. (1.8).

$$T_1/T_2 = \lim_{p_2\rightarrow 0}(p_1/p_2) \approx 1.36609\pm 0.00004, \qquad (1.8)$$

In other words, only in the condition of very low gas pressure, these rules are reliable. Thus,

$$T_2 = (T_1-T_2)/[\lim_{p_2\rightarrow 0}(p_1/p_2)-1] = 273.15K, \qquad (1.9)$$

That means 0℃ equals 273.15K in ideal gas temperature scale.

This is the function of ideal gas temperature scale. The researches show, only in the condition that the gas temperature is much higher than the gas saturation temperature and the gas pressure is very low, the gas property is close to the ideal gas. Thus, the gas thermometer has systematic error, we should pay attention to the suitable conditions.

It seems that ideal gas temperature scale determines the unique thermodynamic temperature. In quite a long time, it was thought to be right. But if we deliberate the problem over, we will find that Eq. (1.6) is a completely artificial setting. It can be proved that the temperature which satisfies the Eq. (1.10) could also be the thermodynamic temperature. There are no reasons to remove them. They are all the examples of thermodynamic temperature.

$$T_1/T_2 = (P_1/P_2)^k, \qquad (1.10)$$

According to the discussion above, it is clear that neither the thermodynamics axioms nor experiments could solve the uniqueness problem of thermodynamic temperature definition and heat definition. The "Twine of temperature and heat" problem is like the problem that "Passing a pot outside a line, how many parallel lines could be drawn", prompts us another way to solve the problem, to find out other thermodynamic temperatures.

The construction of the generalized thermodynamic temperature

Since the thermodynamics axioms could not solve the uniqueness problem of thermodynamic temperature definition and heat definition, is there another definition of the temperature and heat? We propose a hypothesis, the thermodynamic temperature is not unique.

We call this new thermodynamic temperature "the generalized thermodynamic temperature", written as L, the corresponding heat is called the generalized heat, written as Φ, the corresponding entropy is called the generalized entropy, written as Z, and so on.

We think the new thermodynamic physical quantities should have the following properties:

1. The generalized thermodynamic temperature L represents the cold and hot of the objects.

2. The generalized thermodynamic heat Φ satisfies the characters of the classical thermodynamic heat.

3. The generalized thermodynamic entropy Z has all the properties of the classical thermodynamic entropy.

4. The heat engine efficiency of reversible process between two isothermal heat sources could be expressed by the new thermodynamic temperature, and keep the same form as the classical thermodynamics.

5. The rules expressed by the new thermodynamic temperature will not be against to the thermodynamics axioms.

Based on the properties above, the L should be satisfied for Eq. (2.1) and Eq. (2.2),

$$g(L) = T, \qquad (2.1)$$
$$L = g^{-1}(T) = f(T), \qquad (2.2)$$

$f(T)$ is a monotonic and uniform function, for reversible process,

$$d\Phi = LdZ, \qquad (2.3)$$

The heat engine efficiency of reversible process between two isothermal heat sources could be expressed by Eq. (2.4)

$$\eta_{tk} = W/\Phi_1 = (\Phi_1 - \Phi_2)/\Phi_1 = 1 - \Phi_2/\Phi_1 = 1 - L_2/L_1, \qquad (2.4)$$

In other words, $\Phi_2/\Phi_1 = L_2/L_1$ could be the definition formulas of the generalized thermodynamic temperature.

Z, which is denoted as the generalized thermodynamic entropy, is satisfied for the following expression:

$$LZ = f(T) Z = kTS, \qquad (2.5)$$

k is a nonzero real number and is called the thermodynamic temperature transformation ratio.

$$dZ = d[kTS/f(T)], \qquad (2.6)$$

Since,

$$d(kTS) = d[f(T) Z] = f(T)dZ + Zdf(T), \qquad (2.7)$$

Then,

$$LdZ = f(T)dZ = kd(TS) - Zf'(T)dT$$
$$= k(TdS + SdT) - Zf'(T)dT \qquad (2.8)$$

Substitute Eq. (2.5) into Eq. (2.8), we obtain:

$$(1/k) LdZ = TdS + \{1 - T[f'(T)/f(T)]\} SdT, \qquad (2.9)$$

For simplicity, $T[f'(T)/f(T)]$ is defined as $1/k$, k is a nonzero dimensionless real number.

$$T[f'(T)/f(T)] = 1/k(k \neq 0), \qquad (2.10)$$

Then Eq. (2.9) is simplified as

$$LdZ = k[TdS + (1 - 1/k)SdT] = TdS + (k-1) d(TS)$$
$$TdS = LdZ + (1-k) d(TS), \qquad (2.11)$$

Due to the characteristic function, internal energy satisfies the following expression:

$$dU = TdS - pdv, \qquad (2.12)$$

Substitute Eq. (2.11) into Eq. (2.12) and it becomes as

$$dU = [(1-k)/k]d(LZ) + LdZ - pdv, \qquad (2.13)$$

Eq. (2.13) is simplified as

$$d\{U - [(1-k)/k]LZ\} = LdZ - pdv, \qquad (2.14)$$

Define the new thermodynamics state parameter U_k as:

$$U_k = U - [(1-k)/k] LZ, \qquad (2.15)$$

Considering the non-uniqueness of thermodynamics energy, U_k is called the generalized internal energy based on the thermodynamic temperature transformation ratio k. u_k is defined as the specific eneralized thermodynamic internal energy. Here we discuss the relationship between the generalized thermodynamic temperature L and the classical thermodynamic temperature T.

Change Eq. (2.10) into Eq. (2.16),

$$df/f = (1/k)dT/T, \qquad (2.16)$$

Then,

$$\mathrm{In}f = (1/k)\mathrm{In}T + \mathrm{In}c, \tag{2.17}$$

$$f(T) = L = cT^{1/k} \; (k \neq 0), \tag{2.18}$$

For simplicity, set c = 1 and then

$$L = T^{1/k} \; (k \neq 0), \tag{2.19}$$

$$Z = kS/T^{(1-k)/k}, \tag{2.20}$$

In Eq. (2.20) L is the generalized thermodynamic temperature whose thermodynamic temperature transformation ratio is k, called the generalized temperature for short. Z is the generalized thermodynamic entropy whose thermodynamic temperature transformation ratio is k, called the generalized thermodynamic entropy for short. ζ is defined as the specific generalized thermodynamic entropy.

It is not difficult to find that, when T is in the range of positive real numbers, the generalized thermodynamic temperature L determined by Eq. (2.19) has the property of monotone single valued function, so we regard Eq. (2.19) as the definition formulas of generalized thermodynamic temperature.

So could the generalized thermodynamic parameters completely replace the classical thermodynamic parameters? By the analysis below, we can find the answer is yes.

The expression of the first law of thermodynamics in term of the generalized thermodynamic temperature

In the classical thermodynamics, the expression of the first law of thermodynamics is:

$$\delta Q = dU + \delta W, \tag{3.1}$$

For the system with the generalized thermodynamic temperature whose temperature transformation ratio is k, add $-[(1-k)/k] \, LZ$ to both sides of Eq. (3.1).

$$\delta Q - [(1-k)/k] \, d(LZ) = d\{U - [(1-k)/k] \, TS\} + \delta W, \tag{3.2}$$

Define $\Phi_k = Q - [(1-k)/k]LZ$, Φ_k is called the generalized heat based on the thermodynamic temperature transformation ratio k. φ_k is defined as the specific generalized heat based on the thermodynamic temperature transformation ratio k.

Then Eq. (3.2) is simplified as

$$dU_k = \delta\Phi_k - \delta W, \tag{3.3}$$

When the process is reversible, we get

$$d\Phi_k = dU_k + dW, \tag{3.4}$$

Compare Eq. (3.4) with Eq. (2.12), we get

$$d\Phi_k = LdZ, \tag{3.5}$$

Eq. (3.3) is called the general expression of the first law of thermodynamics in generalized thermodynamic temperature.

Obviously, Eq. (3.3) is not only the expression of the first law of thermodynamics with classical thermodynamics temperature like Eq. (3.1) but also the expression of the first law of thermodynamics with different generalized thermodynamic temperature scales.

Eq. (3.5) is the same as Eq. (2.3) which is satisfied for the condition. So the generalized thermodynamic temperature L and generalized thermodynamic entropy Z could completely replace the classical temperature and entropy, and express the first law of thermodynamics without any difficulties. Given all that, we present a new expression of the first law of thermodynamics as follows:

There are different thermodynamic temperatures, they could interconvert into each other. For each thermodynamic temperature, there is corresponding heat, different heat could also interconvert into each other. In the condition of given thermodynamic temperature, the heat of thermodynamic system get from outside, is equal to the sum of the increase of generalized internal energy and the external work.

The generalized Carnot cycle and generalized Clausius inequality, the expression of the second law of thermodynamics in the generalized thermodynamic temperature

Generalized Carnot cycle works between two isothermal heat sources. Two reversible generalized isothermal processes and two reversible generalized entropy processes consist of the generalized Carnot cycle. (Fig. 1).
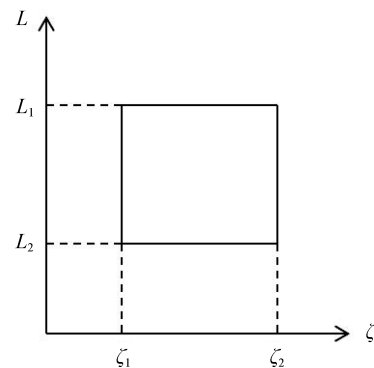

Fig. 1 The thermal process of generalized Carnot cycle.

The generalized heat of reversible process can be deduced from Eq. (3.5):

$$\varphi_{k1} = L_1 \, (\zeta_2 - \zeta_1), \tag{4.1}$$

$$\varphi_{k2} = L_2 \, (\zeta_2 - \zeta_1), \tag{4.2}$$

Since u_k is a state parameter, at the end of cycle process,

$$du_k = 0, \tag{4.3}$$

$$\oint du_k = \oint Ld\zeta - \oint pdv, \tag{4.4}$$

$$\oint pdv = w = \oint Ld\zeta \tag{4.5}$$

$$\eta_{tk} = w/\varphi_{k1} = (\varphi_{k1} - \varphi_{k2}) \, / \varphi_{k1} = 1 - L_2/L_1, \tag{4.6}$$

Eq. (4.6) shows that under the definition of the generalized thermodynamics, the heat efficiency of generalized Carnot cycle still remains the same form as the classical thermodynamics.

After the generalized temperature and the generalized entropy are presented, it is obvious that the first Carnot law should be corrected as follows: " Under the condition of the same generalized temperature scales, any reversible heat engine which works between the same two heat sources has the same heat efficiency; under the condition of different generalized temperature scales, any reversible heat engine which works between the same two heat sources has different heat efficiencies, but there is a one - to - one relationship between each two heat efficiencies with different generalized temperature scales. " The expression not only reflects the essence that the temperature determines the heat efficiency, but also shows the influence of different generalized temperature scales on the heat efficiency. It's not difficult to understand that why the definition of heat efficiency of heat engine changes, the generalized heat has the similar character as the cooling capacity in classical thermodynamics.

$$\Phi_1/\Phi_2 = L_1/L_2, \quad (4.7)$$

Eq. (4.7) is the same as Eq. (1.2)—the definition of temperature scale in the classical thermodynamics in forms. This is why L is called the generalized temperature scale.

Here generalized Clausius inequality will be derived from the generalized Carnot cycle.

As shown from Fig.2, it is noted that $L_0 \geq L$. C is the generalized Carnot heat engine, absorbing heat $d\Phi_0$ from L_0. After doing work dW_c, C exports heat $d\Phi$ with temperature L to the general heat engine A.
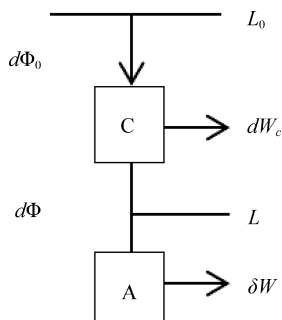

Fig. 2   The generalized Carnot cycle.

For one or more micro generalized Carnot cycles, we have:

$$d\Phi_0/L_0 = \sum_1^{i=n} d\Phi_{0i}/L_0 = \sum_1^{i=n} d\Phi_i/L = d\Phi/L, \quad (4.8)$$

$$dW_c = \sum_{i=1}^n dW_{ci} = \sum_n^{i=1} d\Phi_{0i} - d\Phi_i = d\Phi_0 - d\Phi, \quad (4.9)$$

For the work of the heat engine A:

$$\delta W + dU_{k,A} = d\Phi_k, \quad (4.10)$$

δW is the work done by heat engine A. $dU_{k,A}$ is the generalized internal energy of the heat engine A.

For the general heat engine A, the cycle could be reversible or irreversible. Assume that some micro genera-

lized Carnot cycles correspond a micro A heat engine cycle. After the two heat engines are combined into a new heat engine, we can get:

$$\oint (dW + dW_c) = \oint d\Phi_0 + \oint dU_{k,A}, \quad (4.11)$$

Since

$$\oint dU_{k,A} = 0, \quad (4.12)$$

Then

$$\oint \delta(W + W_c) = \oint (L_0/L)d\Phi, \quad (4.13)$$

$$\oint (d\Phi/L) = (1/L_0)\oint \delta(W + W_c), \quad (4.14)$$

Since the heat engine is a single heat source, according to the second law of thermodynamics, we have:

$$\oint \delta(W + W_c)\delta \leq 0, \quad (4.15)$$

Because

$$T_0 \geq 0, L_0 = T_0^{1/k}, \quad (4.16)$$

Then

$$\oint d\Phi/L \leq 0, \quad (4.17)$$

Eq. (4.17) is the generalized Clausius inequality in generalized temperature scale.

Furthermore, when $\oint d\Phi/L = 0$, the process is reversible, according to Eq. (3.5)

$$d\Phi/L = dZ, \quad (4.18)$$

Substituting Eq. (4.18) into Eq. (4.17), and consider the real process maybe irreversible, we get

$$\oint (dZ - \delta\Phi/L) \geq 0, \quad (4.19)$$

The general condition to make the Eq. (4.19) true is:

$$dZ - \delta\Phi/L \geq 0, \quad (4.20)$$

Define

$$dZ - \delta\Phi/L = \delta Z_e, \quad (4.21)$$

$\delta\Phi/L$ is called the generalized entropy flow, can be positive or negative. δZ_e is called the generalized entropy production, only can be positive.

$$\delta Z_e \geq 0, \quad (4.22)$$

Eq. (4.22) "The generalized entropy production function" is also regarded as the expression of the second law of thermodynamics in generalized thermodynamic temperature.

The generalized entropy equation is:

$$dZ = \delta\Phi/L + \delta Z_e, \quad (4.23)$$

Conclusions

Based on the first law and the second law of thermodynamics and according to the definition of the new thermodynamic temperature scale, a series of new conceptions are proposed in this paper, such as generalized temperature, generalized entropy, generalized heat, generalized internal energy, etc. It is proved that the mathematical relationships of the new conceptions are almost the same forms as the relational expressions of classical thermodynamics.

The expression of the first law of generalized thermodynamics is Eq. (3.3)

$$dU_k = \delta\Phi_k - \delta W, \quad (3.3)$$

The expression of the second law of generalized thermodynamics is Eq. (4.22)

$$\delta Z_e \geq 0, \tag{4.22}$$

For generalized Carnot heat engine, the expression is Eq. (4.7)

$$\Phi_1/\Phi_2 = L_1/L_2, \tag{4.7}$$

The above consequences show that, for different temperature scales, different conceptions of heat, internal energy and entropy can be defined, respectively. From this significance, the conceptions of entropy and heat, etc. are not unique. This paper gives the conversion equations of them.

Otherwise, according to the strict mathematical derivation, the new relationships of the generalized parameters are obtained based on the new temperature scales. Among these, the most fundamental relationship is that: under the condition that $LZ = kTS$, the relationship between the generalized temperature and the classical temperature can be expressed by Eq. (2.19) $L = T^{1/k}$ ($k \neq 0$)— a partial solution of Eq. (2.10) $T[f'(T)/f(T)] = 1/k$ ($k \neq 0$)

(k is nonzero real).

The new conceptions and their relational expressions of the thermodynamics may support different views and thoughts for researchers to make further efforts to understand thermodynamics.

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